

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/GB05/001231

International filing date: 30 March 2005 (30.03.2005)

Document type: Certified copy of priority document

Document details: Country/Office: GB
Number: 0407114.8
Filing date: 30 March 2004 (30.03.2004)

Date of receipt at the International Bureau: 12 May 2005 (12.05.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



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2. Patent application number <i>(The Patent Office will fill in this part)</i>	0407114.8
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3. Full name, address and postcode of the or of each applicant <i>(underline all surnames)</i>	COLORMATRIX EUROPE LTD 9-11 Unity Grove, Knowsley Business Park, Knowsley, Merseyside, L34 9GT.
Patents ADP number <i>(if you know it)</i>	6985329003
If the applicant is a corporate body, give the country/state of its incorporation	ENGLAND
4. Title of the invention	POLYMER ADDITIVES AND METHODS OF USE THEREOF.
5. Name of your agent <i>(if you have one)</i>	W.P.THOMPSON & CO. "Address for service" in the United Kingdom Coopers Building, Church street, Liverpool, L1 3AB Applicant fees 15 Clare Road Halifax HX1 2AY 190001
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- 1 -

DESCRIPTION

POLYMER ADDITIVES AND METHODS OF USE THEREOF

The present invention relates to polymer compositions having improved reheat properties, the use of such compositions, and to a method of production thereof. The invention also concerns a polymer reheat additive which can be used with polymers and which may be useful when applied to thermoplastic polymers, especially those used in the field of container manufacturing.

Polymers are often used in producing preforms (parisons) which are heated with infrared heating lamps prior to being blow-moulded into articles, including liquid containers such as beverage bottles and the like. The heat lamps used for reheating polymer preforms (parisons) for the commercial manufacture of liquid containers such as beverage bottles are typically quartz lamps having a broad light emission spectrum from 500 nm to greater than 1500 nm, i.e. infrared heating lamps. The maximum light emission from these lamps occurs typically in the range of about 1100 to 1300 nm. Polyester, especially polyethylene terephthalate ("PET"), absorbs poorly in the region between 500 to 1400 nm. Thus, in order to speed up the reheat step in bottle production, or to reduce the amount of energy required for reheat, agents which absorb light in the region between 700 to 1300 nm can be added to the polyester polymer as reheat additives.

A variety of black and grey body absorbing compounds have previously been used as reheat agents to improve the rate of heating characteristics of polyester under infrared

heating lamps. These compounds are typically black iron oxide, elemental antimony, black carbon and copper chromite. The term 'black carbon' includes graphite, any form of carbon black, charcoal, activated carbon and the like. However, these materials all have greater intrinsic absorptivity in the visible spectrum between 400 and 700 nm than in the infrared region between 700 and 1400 nm. This makes these materials appear inefficient when the visible impact versus infrared absorptivity is considered. High levels of reheat cannot be achieved without the severe darkening of the polymer. While the impact of these materials on the visual appearance of preforms can be reduced by using relatively large particles of these additives, they inherently cannot exhibit greater absorptivity in the infrared region of the electromagnetic spectrum relative to the visible region of the spectrum. Therefore, the amount of absorbing materials that can be added to a polymer is limited by the impact of those materials on polymer visual properties, such as transparency. This is particularly pertinent if the preforms are to be used to manufacture liquid containers such as beverage bottles, especially for use in containing mineral water, where high transparency and an absence of colour are considered essential. Transparency is usually represented as "L*" in the CIELAB system, with 100 being the highest and 0 being the darkest. Generally, darker colored reheat agents can be added in only very small quantities because of their negative impact on L*.

It is therefore an object of the present invention to alleviate one or more of the above identified problems. Furthermore, it would be desirable to provide an infrared absorbing material which can be added to a thermoplastic moulding composition in a concentration sufficient effectively to increase the reheat rate of the polymer, yet have a reduced impact

on the lightness compared to traditional reheat agents. It would be most preferable to effectively increase the reheat rate of the moulded composition by up to 20 percent. It would also be advantageous to have neutrally coloured preforms. Therefore, a reheat aid that imparts a blue colour would be particularly advantageous as it could be used to tone away the undesirable intrinsic yellow colour acquired by polymers, such as PET, as they are formed.

The present invention may also be useful in any other application known or yet to be developed in which the heating of polymers using infrared heating lamps is required.

According to the present invention there is provided a polymer reheat additive comprising an inorganic material having greater intrinsic absorptivity in the infra red region of the spectrum (between 700 and 1400nm) than in the visible region of the light spectrum (between 400 and 700nm).

Also according to the present invention there is provided a polymer reheat additive comprising an inorganic material having at least one absorption maximum in the infra red region of the spectrum (between 700 and 1400nm) which is greater than any absorption maximum in the visible region of the spectrum (between 400 and 700nm).

The invention also provides a thermoplastic moulding composition comprising a reheat additive as described above. Also provided in accordance with the invention is a moulded article formed from such a moulding composition.

In accordance with the present invention, there is provided a polymer additive for improving the reheat characteristics of a polymer or polymeric composition, the additive comprising an inorganic material that is not any form of black carbon, metallic antimony, iron oxide or copper chromite.

It has been discovered that certain inorganic additive materials can be useful in reheat applications. Particular materials which are suitable for use as reheat additives, and certain of their physical and/or chemical characteristics will be described below.

Preferably, the inorganic materials useful as reheat additives absorb light in the infra red region, are compatible with thermoplastic moulding compositions, are non-toxic and have an aesthetically neutral or positive impact on the colour of a moulded article formed from a composition to which they are added.

The invention further provides a thermoplastic moulding composition comprising a polyester, and at least one reheat additive being an inorganic material other than any form of black carbon, metallic antimony, iron oxide or copper chromite, the reheat additive being present in the composition in an amount effective to absorb light in the infra red region and thus reduce the energy requirement for reheating to a blow moulding temperature an article moulded from the composition.

Therefore, the additive of the present invention allows a polymer to have an improved reheat characteristic, wherein the polymer reheats and therefore attains a temperature

above its glass transition temperature quicker and as reheat times are reduced and productivity is thus increased. The additive thus allows for more efficient handling of the polymer.

The polymer may comprise polymer particles, with the additive dispersed throughout the polymer particles. Alternatively, the polymer may be a solid or fragmented with the additive disposed within the polymer. The additive may comprise colloids or particles, but will preferably comprise nanoparticles. Nanoparticles as referred to herein are particles with an average particle diameter less than 1 micron, preferably less than 100 nm.

There are two general types of inorganic materials that fall within the scope of this invention. The first type of materials (type 1) are those that intrinsically exhibit greater absorptivity between 700 and 1400 nm than between 400 and 700 nm. Absorptivity is calculated by measuring the absorbance of a polyester plaque containing the material at 400, 700 and 1100 nm and then determining the percentage change in absorption that occurs between 400 and 700 nm and then 700 to 1100nm. The materials that fall within the scope of this invention have a % absorptivity in the region 700 to 1100nm that is greater than the % absorptivity in the region 400 to 700 nm and is positive in value. A particularly preferred example of such an inorganic material is reduced indium tin oxide. Intrinsic absorptivity, as used herein, should be taken to be the absorbance exhibited by a particle of the said material when the particle size is sufficiently small that a significant amount of the impinging light is transmitted at every wavelength.

The additional type of materials (type 2) are those that have a greater absorption maximum in the region between 700 to 1400 nm than the average absorption between 400 and 700nm. The absorption can be that directly measured by a spectrophotometer. A particularly preferred example of such an inorganic material is titanium nitride.

The inorganic materials of the present invention can be of either type as herein described above. Preferably, the additive is capable of increasing energy absorption of the polymer in the near-infra red light range. It will be apparent to one skilled in the art that this range of the spectrum is 700 to approximately at least 1400 nm. More preferably, the additive is capable of increasing energy absorption of the polymer in the near-infra red light range than it does the visible light range (400 and 700nm). Preferably the inorganic material exhibits a greater absorptivity in the region between 700 and 1400 nm than between 400 and 700 nm of at least 10%, more preferably at least 25%, and much more preferably at least 50% and yet more preferably still at least 100%.

It is preferred that the additive has an average energy absorption maximum in the range of 700 to 1400 nm that is greater than the average energy absorption in the range of 400 and 700nm. Preferably, the average energy absorption maximum in the region between 700 to 1400 nm that is greater than the average absorption in the region between 400 to 700 nm is at least 1% greater, more preferably still at least 5% greater and much more preferably still at least 10% greater. It is most preferable that the average absorption maximum is at least 50% greater.

The average particle size of additive that may be used to increase the absorption of energy between 700 and 1400 nm may be less than 10 microns, preferably less than 1 micron and more preferably less than 100 nm. Preferably, the particle size of the inorganic material is less than that sufficient size to cause at least 99% absorption of light between 700 and 1400 nm impinging on a particle. Preferably the particle size of the inorganic material is less than that sufficient size to cause at least at least 90% and more preferably at least 50% absorption of light between 700 and 1400 nm impinging on a particle.

If the particles are too large, they will absorb all of the impinging light in both the visible and infrared portions of the spectrum, and will thus provide no preferential absorption of infrared radiation. As the particle size is reduced, the relative absorption difference between the visible and infrared portions of the spectrum will increase until the intrinsic absorptivity is achieved. Hence, selection of the preferred particle size for each additive will be dependent on the specific absorptivity of that compound in the visible and infrared portions of the electromagnetic spectrum. It will be understood that if the particles are large enough to absorb more than 99% of the impinging infrared radiation, then higher loadings will be necessary to achieve the same amount of reheat improvement than with particles that absorb 90% or less of the impinging infrared radiation. It is anticipated that the most suitable particles will be nanoparticles. Nanoparticles being particles with an average particle size less than 1 micron. A preferred average particle size is less than 100nm.

The additive may have even or flat absorption characteristics across the visible region of the spectrum with negligible absorption minima and maxima. This would be desirable if a neutral or un-coloured plastics material is required, e.g. mineral water bottles. However, the additive may also have uneven or slanted absorption characteristics across the visible region of the spectrum possessing significant absorption minima or maxima. This would be desirable for the production of coloured bottles. An additive imparting a blue colour to the preform is especially desirable as it can act as not only to improve the reheat profile of the polymer, but also to colour the resulting plastics material. Polymers, particularly polyesters such as poly(ethylene terephthalate), are known to yellow upon exposure to elevated temperatures. Indeed poly(ethylene terephthalate) yellows as it is being manufactured. It may therefore be necessary to add a toner to the polyester to adjust its colour from a yellow back to a neutral shade. These toners are thus usually colorants that impart a blue shade, a typical example being cobalt acetate. Therefore additives that impart a blue shade to the preform will also make good toners and are especially desirable. However, additives that give rise to other visual colours can also be used as when used in conjunction with a complimentary coloured toning agent, usually a traditional colorant, a neutral shade can easily be achieved. A particularly preferred inorganic material of the present invention being titanium nitride, which imparts a blue colour having an absorption minimum in the visible region around 475 nm.

The additive may be produced from a number of inorganic materials, and one skilled in the art of material science would be able not only to identify suitable materials to effect

the required goal, but will also be able to develop new or adapt existing compounds and materials. Preferably, the material is selected from one or more of the following group of materials: elemental metals, metalloids, oxides, doped oxides, mixed oxides, nitrides, silicides or boride compounds. Suitable materials for the additive may be selected from one or more of the following group of materials: titanium nitride, zirconium nitride, indium tin oxide, reduced indium tin oxide, antimony tin oxide, gold, silver, molybdenum or tantalum.

The polymer additive may further comprise one or more additional materials to assist reheat characteristics of the polymer. Additionally or alternately, the polymer additive may further comprise one or more additional materials to influence the characteristics of the polymer. For example, one or more black or grey body infrared absorbing materials may be incorporated with the additive which can result in the absorption of more near-infrared radiation greater than 700nm. Such black body or grey body infrared absorbing material may comprise black carbon, iron oxides, copper chromite or metallic antimony formed by the reduction of antimony trioxide during the polymerisation reaction. Other materials may include colourants etc. The additive may also be used in conjunction with organic materials, such as near-infrared dyes, that have an absorption maximum in the region 700 to 1400 nm.

The polymer can essentially be any polymer which is used to produce a plastics material, but preferably, the polymer comprises a thermoplastic polymer (including both polymers that are synthetic or natural). It will be evident to one skilled in the art that such a

thermoplastic polymer will have an application for injection moulding of articles such as containers preforms and the like. Preferably, the thermoplastic polymer is selected from one or more of the following groups of polymers: polyesters, polycarbonates, polyamides, polyolefins, polystyrenes, vinyl polymers, acrylic polymers and copolymers and blends thereof. Preferred polymers are polyesters as used by liquid containers and particularly beverage bottles such as poly(ethylene terephthalate) or a copolymer thereof. The polymers with the additive can be used in producing preforms such as container preforms before the preforms are heated or inserted in to a stretch-blow moulding machine. The invention can be used in any polymer where increasing the rate of heat uptake using infrared heating lamps would be advantageous.

Polyethylene terephthalate used for injection moulding purposes is typically post-condensed and has a molecular weight in the region of about 25,000 to 30,000. However, it has also been proposed to use a fibre grade polyethylene terephthalate which is cheaper but is non-post-condensed, with a lower molecular weight in the region of about 20,000. It has further been suggested to use copolymers of polyethylene terephthalate which contain repeat units from at least 85 mole % terephthalic acid and at least 85 mole % of ethylene glycol. Dicarboxylic acids which can be included, along with terephthalic acid, are exemplified by phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid and sebacic acid. Other diols which may be incorporated in the copolymers, in addition to ethylene glycol, include diethylene glycol, triethylene glycol, 1,4-cyclohexanediethanol, propane-1,3-diol,

butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentane-2,4-diol, 2-methylpentane-1,4-diol, 2,2,4-trimethylpentane-1,3-diol, 2-ethylhexane-1,3-diol, 2,2-diethylpropane-1,3-diol, hexane-1,3-diol, 1,4-di(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, and 2,2-bis-(4-hydroxypropoxyphephenyl)-propane. In this specification the term "polyethylene terephthalate" includes not only polyethylene terephthalate but also such copolyesters.

Injection moulding of polyethylene terephthalate and other polyester moulding compositions is typically carried out using an injection moulding machine and a maximum barrel temperature in the range of from about 260 °C to about 285 °C or more, for example, up to about 310 °C. The dwell time at this maximum temperature is typically in the range of from about 15 seconds to about 5 minutes or more, preferably from about 30 seconds to about 2 minutes.

In a preferred embodiment of the present invention, the additive is capable of increasing the percentage of reheat per unit of lightness lost ratio than an equivalent preform made from a polymer containing a traditional black or grey body absorbing agent such as any form of black carbon or metallic antimony formed by the reduction of antimony trioxide.

In accordance with another aspect of the present invention, there is provided a method of improving the reheat characteristics of a polymer by adding an inorganic material to the

polymer prior to reheating, said inorganic material not being black carbon, metallic antimony, iron oxide or copper chromite.

The method may utilize an additive as herein described above. Polymers containing the additive will be particularly suited for use in injection moulding of articles. Furthermore, the additive may be dispersed in a liquid. Should the additive be dispersed in a liquid then the liquid can be applied to the polymer at the polymerization stage or the injection moulding stage. Such an article could potentially be any article which can be injection moulded. Preferably, the article is a preform that can then be stretch-blow moulded into a liquid container such as beverage bottles using infrared heating lamps.

The inorganic material can be mixed with the monomers at the start of or during the polymerization reaction or to produce pre-made polymer pellets during an injection moulding process. A particularly preferred injection moulding process being the production of container preforms, which are to be heated with infrared heating lamps prior to stretch blow moulding into a liquid container such as beverage bottle.

The inorganic material may be added directly in the form of a powder. The particles of the inorganic material can also be added in the form of a liquid dispersion. The liquid carrier can be a vegetable or mineral oil or a glycol. A particularly preferred glycol is ethylene glycol, especially if the particles of inorganic material are to be added to a PET polymerization reaction mixture. It is also advantageous if the inorganic material is

milled in the liquid carrier. Milling serves to break down any agglomerates present into primary particles.

Other components such as surfactants, thickening and stabilizing agents may be added to improve the liquid dispersion system of the present invention.

Other polymer additives may also be included in the liquid dispersion system of the present invention such as slip property modifiers, acetaledehyde removing agents, IV modifiers, barrier agents such as Amosorb[®], flame retardancy agents, surface finish modifiers and conductivity modifiers.

In accordance with a further aspect of the present invention, there is provided an article made from a polymer containing the additive of inorganic material that intrinsically exhibits greater absorptivity between 700 and 1400 nm than between 400 and 700 nm. In yet another aspect of the present invention, there is provided an article made from a polymer containing the additive of inorganic material that has a greater absorption maximum in the region between 700 to 1400 nm than the average absorption between 400 and 700nm. A particularly preferred article may be a container preform. An especially preferred container preform being one which can be heated with infrared heating lamps prior to being stretch-blow moulded into a liquid container such as a beverage bottle. The types of beverage such bottle can contain includes but is not limited to beer, fruit juice, carbonated and still mineral water and other carbonated soft drinks such as Coca-Cola[®].

In accordance with yet a further aspect of the present invention, there is provided a method of increasing the reheat characteristics of a polymer, comprising the incorporation into the polymer particles of at least one inorganic material, such that the polymer has a greater % reheat per unit of lightness lost ratio than an equivalent polymer containing a traditional black or grey body absorbing agent such as black carbon or metallic antimony formed by the reduction of antimony trioxide or iron oxide or copper chromite.

An additional aspect of the present invention provides for the use of an inorganic material (not being black carbon, a metallic antimony, iron oxide or copper chromite) to improve the reheat properties of a polymer or polymeric composition.

In yet a further aspect of the present invention, there is provided a moulded article formed from a polymer or polymeric composition mixed with an inorganic additive (not being black carbon, metallic antimony, iron oxide or copper chromite).

In a number of the aspects of the invention, the inorganic material/additive may be selected from one or more of the following group of materials: titanium nitride, zirconium nitride, indium tin oxide, reduced indium tin oxide, antimony tin oxide, gold, silver, molybdenum or tantalum. The inorganic material/additive is a nanoparticle having an average particle size less than 1 micron. Preferably, the average particle size of the inorganic material/additive is 100 nm or less. The polymer or polymeric composition is

selected one or more of the following groups from the group of polymers: polyesters, polycarbonates, polyamides, polyolefins, polystyrenes, vinyl polymers, acrylic polymers and copolymers and blends thereof. The article produced from a polymer comprising the polymer and inorganic material/additive is preferably injection moulded. Where the article is a container preform, said preform is preferably used in a stretch-blow moulding process requiring a heating step with infrared heating lamps, to produce bottles suitable for use in containing liquids such as beverages.

The invention will now be shown by way of example only with reference to the figures and the following examples, in which:

Figure 1 illustrates the effect that an additive in accordance with the present invention has on a polymer by means of transmission spectrum. The Figure shows 60 nm particles of titanium nitride in PET, and for comparison the transmission spectrum for the commercially available reheat polymer CB11e (Voridian) which contains a prior art infrared absorbing additive. Also shown is the transmission spectrum of a PET polymer (9921W) that does not contain an infrared-absorbing reheat additive. Another example a compound that exhibits greater absorptivity in the infrared compared to the visible spectrum is reduced indium tin oxide; and

Figure 2 shows transmission spectrum for an additive in accordance with the present invention comprising 40nm particles of reduced indium tin oxide.

EXAMPLES

Preforms were made using a 160-ton HUSKY injection moulding machine which made two preforms per shot. Each preform weighed approximately 34 grams and was cylindrical, approximately 130mm in length with a screw top base. These preforms could be blown into one-litre bottles with a petaloid base.

Polyester injection moulding took place at 270°C. General purpose poly(styrene) injection moulding took place at 200°C.

The polymers used were:

B60 (DuPontSA) – a commercial, bottle grade resin PET resin, toned and non-reheat.
Untoned B60 (DuPontSA) the same as B60 but without any toning therefore showing the natural yellow colour of the resin.

9921W (Voridian) - a commercial, bottle grade resin PET resin, toned and non-reheat.

Laser+ (DuPontSA) – a commercial bottle grade reheat resin.

CB11e (Voridian) – a commercial bottle grade reheat resin.

General purpose poly(styrene) (GPS).

CB11e and Laser+ are both reheat resins containing metallic antimony as the reheat aid. CB11e, has approximately twice the reheat but has approximately twice the reduction in lightness as Laser+.

Where the inorganic particle compound was milled milling took place as follows: The inorganic particle compound (5g) was stirred into an oil known to those skilled in the art to be compatible with the polymer the inorganic particles are to be incorporated into (total mass of oil and particle mixture = 50g). The oil and particle mixture was then transferred to a 100ml glass jar approximately 55% filled with small glass beads (1.2 mm diameter). The glass jar was shaken at 600 shakes per minute on a Red-Devil paint shaker. The milled dispersion was used immediately.

The following inorganic particle compounds were used as reheat aids.

1. Titanium nitride, average primary particle size 60nm and 30nm, supplied by Neomat of Riga, Latvia.
2. Reduced indium tin oxide, average primary particle size less than 40nm, was supplied by NanoProducts Corp. Longmont, Co., USA.
3. Antimony tin oxide, average primary article size of 30nm was supplied by NanoPhase Technologies, Romeoville, Il, USA.
4. Lanthanum hexaboride nanopowder, average primary particle size less than 40nm, was supplied by NanoProducts Corp. Longmont Co., USA.

5. Cobalt silicide (CoSi_2) powder of average particle size 1000nm was supplied by Alfa-Aesar.

The near infrared dye employed was supplied by ADS Dyes, Toronto, Canada. The Lamp Black 101 (carbon black) was supplied by Degussa. Sigma-Aldrich supplied all other materials.

The particles of inorganic materials were mixed into the pre-made polymer pellets by placing the powder or liquid dispersion of particles of inorganic material into a bucket fitted with a lid containing the hot, dried polymer pellets and then shaking the bucket by hand to mix the two together. The polymer pellets and particles of inorganic material mixture were then immediately used to make preforms by an injection moulding process.

1. Preforms

EXAMPLE 1

TiN milled 60nm at 25ppm in B60 resin.

EXAMPLE 1a

TiN milled 60nm at 25ppm in 9921W resin.

EXAMPLE 1b

TiN milled 30nm at 25ppm in 9921W resin.

EXAMPLE 2

TiN milled at 5ppm in untoned B60 resin.

EXAMPLE 3

TiN milled at 10ppm in untoned B60 resin.

EXAMPLE 4

LaB₆ powder at 100ppm in B60 resin.

EXAMPLE 5

LaB₆ milled at 100ppm in B60 resin.

EXAMPLE 6

ITO powder at 100ppm in B60 resin.

EXAMPLE 6a

ITO powder at 100ppm in 9921W resin.

EXAMPLE 7

ITO milled resin at 100ppm in B60 resin.

EXAMPLE 8

ATO powder at 463ppm in B60 resin.

EXAMPLE 9

ATO milled at 100ppm in B60 resin.

EXAMPLE 10

TiN milled at 10ppm and ITO milled at 10ppm in untoned B60 resin.

EXAMPLE 11

TiN milled at 10ppm and near-infrared organic dye at 50ppm in untoned B60 resin.

EXAMPLE 12

TiN milled at 10pm and tantalum nanopowder at 100ppm in untoned B60.

EXAMPLE 13

TiN milled at 5ppm and ITO milled at 75ppm in untoned B60 resin.

EXAMPLE 14

TiN milled at 10ppm and ITO milled at 50ppm in untoned B60
resin.

EXAMPLE 15

Mo nanosized powder at 250ppm into B60 resin.

EXAMPLE 16

Cobalt silicide at 100ppm into B60 resin.

Example 17

ITO milled at 100ppm in GPS.

Example 18

TiN milled at 25ppm in GPS.

The colours of the preforms were measured using a Minolta cm-3700d spectrophotometer (D₆₅ illumination, 10° observer, specular included, UV included) linked to an IBM compatible PC.

The preform reheat tests were performed by measuring the room temperature-temperature of a preform using a Raytek MiniTemp laser digital infrared thermometer and then placing it into a stretch blow-moulding bottle machine with a single preform fitting, with all nine Philips IRK halogen infrared heating lamps set to 75% power. The preforms were heated for 35 seconds after which time the temperature of the preform was recorded. The spectral energy distribution of the lamps fitted into this machine is displayed in figure 1. The temperature difference (temperature after 35 seconds of heating minus the room temperature-temperature of the preform) was then used to calculate % change in reheat relative to non-reheat control (either B60 or untoned B60).

EXAMPLE 19

Formulation of inorganic particles in ethylene glycol suitable for adding directly to a polyester polymerization reaction.

Reduced indium tin oxide (5g) or titanium nitride (5g) was stirred into ethylene glycol (up to 50g) and added to a glass jar 50% filled with small glass milling beads (~1.2mm in diameter). The jar was sample was milled by shaking it on the Red-Devil paint shaker at 600 s.p.m. for 10 minutes. The sample was then ready for adding directly to a polyester polymerization reaction mixture.

RESULTS

1. Preform colours

	L	a	b	C	h°
B60	78.96	-0.69	1.61	1.75	113.3
Untoned B60	80.82	-0.47	3.25	3.28	98.2
9921W	77.19	-0.89	4.52	4.6	101.2
Laser+	70.25	-0.27	0.84	0.88	107.6
CB11e	60.54	-0.96	2.66	2.83	109.9
Example 1	64.03	-3.33	-4.10	5.29	230.9
Example 1a	63.12	-2.89	-3.87	5.01	215.3
Example 1b	54.47	-4.51	-7.20	8.50	237.9
Example 2	77.40	-1.15	0.96	1.50	140.2
Example 3	73.62	-1.89	-0.37	1.93	191.0
Example 4	70.64	-0.46	7.33	7.34	93.6
Example 5	67.88	-1.67	6.69	6.89	104.1
Example 6	76.63	-0.60	6.56	6.59	95.2
Example 6a	74.89	-0.59	8.35	8.37	94.0
Example 7	76.46	-0.67	8.82	8.84	94.4
Example 8	63.83	0.95	14.3	14.3	86.2
Example 9	75.85	-0.78	6.76	6.80	96.55
Example 10	73.66	-1.86	0.07	1.86	177.9
Example 11	69.78	-5.02	13.51	14.4	110.4

Example 12	66.48	-1.34	0.50	1.43	159.4
Example 13	74.32	-1.22	5.57	5.70	102.3
Example 14	72.44	-1.84	1.74	2.54	136.7
Example 15	66.22	-0.57	1.10	1.24	117.3
Example 16	76.08	-1.08	3.20	3.38	108.7
GPS	85.50	-0.08	0.68	0.68	96.92
Example 17	83.43	-0.20	4.31	4.31	92.7
Example 18	71.62	-2.03	-5.22	5.60	248.7

2. Reheat versus lightness

	% Reheat	%Reheat / Unit of lightness lost
B60	0	0
Untoned B60	0	0
9921W	0	0
GPS	0	0
Laser+	7.5	0.80
CB11e	17.0	0.92
Example 1	16.8	1.05
Example 1a	16.9	1.20
Example 1b	22.3	0.91
Example 2	18.0	0.99

Example 3	5.4	0.74
Example 4	14.0	0.61
Example 5	15	1.35
Example 6	16.9	6.76
Example 6a	17.0	7.39
Example 7	18.1	7.24
Example 8	17.9	1.18
Example 9	2.0	0.64
Example 10	9.6	1.32
Example 11	10.3	0.92
Example 12	11.2	0.78
Example 13	17.1	2.71
Example 14	16.9	2.13
Example 15	16.5	1.30
Example 16	5.7	1.11
Example 17	18.2	8.79
Example 18	12.7	0.91

In every case the inorganic material reheat aid system has been able to increase the % reheat of the control resin it was incorporated into and as heating was for a fixed time of 35 seconds thus the rate of reheat was increased. Indeed in several instances not only was there an increase in reheat over the control but the % reheat per unit of lightness lost ratio was higher than the preforms made from both of the two commercial reheat resins. This

gave rise to preforms with the same reheat as the two commercial reheat standard but a higher lightness value thus making them desirable for use by the mineral water bottle industry.

Type one inorganic materials - Absorptivity determination

Absorptivity was determined by measuring the absorbance of plaques containing the particles of inorganic material as follows.

Plaques were prepared using a 22-ton BOY injection moulding machine that produces plaques measuring 75 x 50 mm, of two thicknesses, 2 and 2.5 mm.

Plaques were prepared of 9921W containing reduced indium tin oxide (powder) at 100ppm. Control, CB11e and Laser+ plaques were also prepared.

The spectrum of the plaques in the region 300 to 1100 nm was measured using a Perkin-Elmer Lambda 35 uv-vis spectrophotometer linked to an IBM compatible PC.

Absorptivity was then calculated by determining the % change in measured absorbance that occurs across the visible region 400 to 700 nm, and then in the near infrared region 700 to 1100nm. This was perform as follows:-

$$((\text{Abs}_{\lambda_2} - \text{Abs}_{\lambda_1}) / \text{Abs}_{\lambda_1}) * 100$$

Where Abs 1 and 2 are the absorption at either 400, 700 or 1100 nm with $\lambda 2$ always being greater than $\lambda 1$, i.e. when $\lambda 1 = 400$ nm then $\lambda 2 = 700$ nm and when $\lambda 1 = 700$ nm then $\lambda 2 = 1100$ nm.

	Absorptivity % 400 to 700 nm	Absorptivity % 700 to 1100 nm
9921W	-67	-13
Laser+	-33	0.00
CB11e	-35	-1
ITO	-72	+45

Type two inorganic materials – absorbance measurement

A plaque of 9921W was prepared containing TiN (30nm at 15ppm) as above.

The plaques were used to generate spectrophotometer data. The average absorbance over the range 400 to 700 nm and the maximum absorbance in the range 700 to 1100 nm was determined. The % difference between the two was calculated.

	700-1100max	400-700ave	diff.	% diff
9921W	0.0661	0.103031	-0.03693	-35
Laser+	0.1202	0.137931	-0.01773	-13
CB11e	0.1877	0.212215	-0.02452	-12
TiN	0.2463	0.228938	0.17362	+8

CLAIMS

1. A polymer additive for improving the reheat characteristics of a polymer or polymeric composition, the additive comprising an inorganic material that is not black carbon, iron oxide, copper chromite or metallic antimony, said additive being present with the polymer prior to reheating.
2. A polymer additive as claimed in claim 1, wherein the polymer comprises polymer particles.
3. A polymer additive as claimed in either claim 1 or 2, wherein the additive is colloidal or nanoparticulate matter.
4. A polymer additive as claimed in any preceding claim, wherein the additive is capable of increasing energy absorption of the polymer in the range of 700 to 1400 nm.
5. A polymer additive as claimed in claim 4, wherein the additive has an average energy absorption maximum in the range of 700 to 1400 nm that is greater than the average energy absorption in the range of 400 and 700nm.
6. A polymer additive as claimed in either claim 4 or 5, wherein where the additive comprises particles, the size of which is used to increase the absorption of energy between 700 and 1400 nm.

7. A polymer additive as claimed in any of claims 3 to 6, wherein the average particle size of the additive is 100 nm or less.
8. A polymer additive as claimed in any preceding claim, wherein the additive is produced from a material selected from one or more of the following group of materials: elemental metals, oxides, doped oxides, mixed oxides, nitrides, silicides or boride compounds.
9. A polymer additive as claimed in any preceding claim, wherein the additive is produced from a material selected from one or more of the following group of materials: titanium nitride, zirconium nitride, indium tin oxide, reduced indium tin oxide, antimony tin oxide, gold, silver, molybdenum or tantalum.
10. A polymer additive as claimed in any preceding claim, wherein the additive further comprises one or more colourants.
11. A polymer additive as claimed in any preceding claim, wherein the additive further comprises one or more black or grey body infrared absorbing materials.
12. A polymer additive as claimed in claim 11, wherein the black body or grey body infrared absorbing material is comprises black carbon, metallic antimony, iron oxide or copper chromite.

13. A polymer additive as claimed in any preceding claim, wherein the polymer comprises a thermoplastic polymer.
14. A polymer additive as claimed in claim 13, wherein the thermoplastic polymer is selected one or more of the following groups from the group of polymers: polyesters, polycarbonates, polyamides, polyolefins, polystyrenes, vinyl polymers, acrylic polymers and copolymers and blends thereof.
15. A polymer additive as claimed in either claim 13 or 14, wherein the polymer is poly(ethylene terephthalate) or a copolymer thereof.
16. A polymer additive as claimed in any preceding claim for use in producing container performs.
17. A polymer additive as claimed in claim 16, wherein the additive gives rise to a preform with a higher % reheat per unit of lightness lost ratio than an equivalent preform made from a polymer containing black carbon, iron oxide, copper chromite or metallic antimony formed by the reduction of antimony trioxide.

18. A method of improving the reheat characteristics of a polymer by adding an inorganic material to the polymer prior to reheating, said inorganic material not being black carbon, metallic antimony, iron oxide or copper chromite.
19. A method as claimed in claim 18, wherein the additive comprises an additive as claimed in any of claims 1 to 17.
20. A method as claimed in either claim 18 or claim 19, wherein the method is used for injection moulding articles.
21. A method as claimed in any of claims 18 to 20, wherein the polymer and/or the additive is dispersed in a liquid.
22. A method as claimed in claim 21, wherein liquid can be applied to the polymer at the polymerization stage or the injection moulding stage.
23. A method as claimed in any of claims 20 to 22, wherein the article is a container preform.
24. A method as claimed in claim 23, wherein the container preform is stretch blow moulded using infrared heating lamps to form a container suitable for holding liquids.

25. A method as claimed in claim 24, wherein the stretch blow moulded container suitable for holding liquids is a beverage bottle.
26. The use of an inorganic material (not being black carbon, metallic antimony, iron oxide or copper chromite) to improve the reheat properties of a polymer or polymeric composition.
27. The use of an inorganic material as claimed in claim 26, wherein the inorganic material is a material selected from one or more of the following group of materials: titanium nitride, zirconium nitride, indium tin oxide, reduced indium tin oxide, antimony tin oxide, gold, silver, molybdenum or tantalum.
28. The use of an inorganic material as claimed in either claim 26 or 27, wherein the average particle size of the inorganic material is 100 nm or less.
29. The use of an inorganic material as claimed in any of claims 26 to 28, wherein the polymer or polymeric composition is selected from one or more of the following groups of polymers: polyesters, polycarbonates, polyamides, polyolefins, polystyrenes, vinyl polymers, acrylic polymers and copolymers and blends thereof.
30. A thermoplastic moulding composition as claimed in claim 29, wherein the inorganic material is a material selected from one or more of the following group of materials:

titanium nitride, zirconium nitride, indium tin oxide, reduced indium tin oxide, antimony tin oxide, gold, silver, molybdenum or tantalum.

31. A thermoplastic moulding composition as claimed in claim 30, wherein the average particle size of the inorganic material is 100 nm or less.

32. A thermoplastic moulding composition as claimed in any of claims 30 to 31, wherein the thermoplastic plastic polymer is selected one or more of the following groups of thermoplastic plastic polymers: polyesters, polycarbonates, polyamides, polyolefins, polystyrenes, vinyl polymers, acrylic polymers and copolymers and blends thereof.

33. A moulded article formed from a polymer or polymeric composition mixed with an inorganic additive (not being black carbon, metallic antimony, iron oxide or copper chromite).

34. A moulded article as claimed in claim 33, wherein the moulded article is injection moulded.

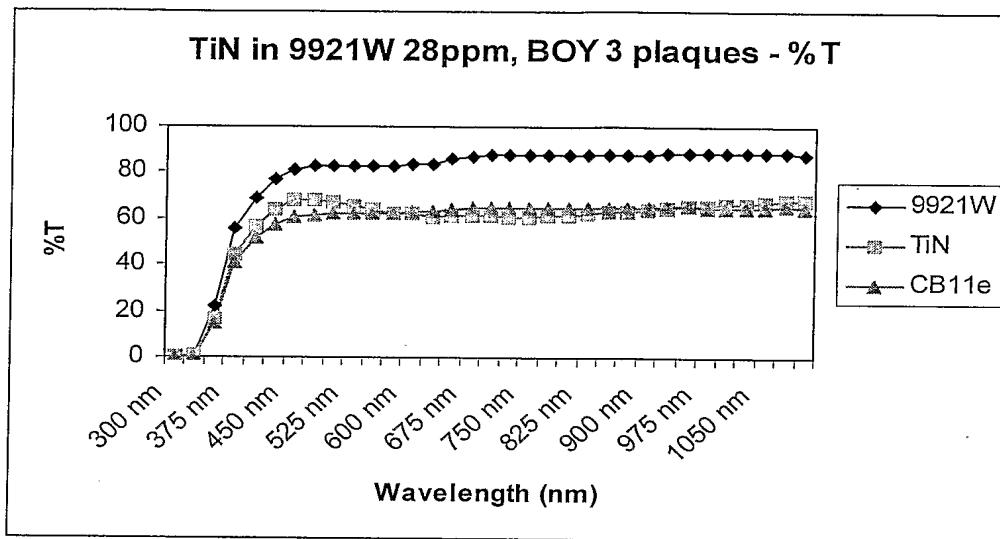
35. A moulded article as claimed in either claim 33 or 34, wherein the inorganic material is a material selected from one or more of the following group of materials: titanium nitride, zirconium nitride, indium tin oxide, reduced indium tin oxide, antimony tin oxide, gold, silver, molybdenum or tantalum.

36. A moulded article as claimed in any of claims 33 to 35, wherein the polymer or polymeric composition is selected one or more of the following groups of polymers: polyesters, polycarbonates, polyamides, polyolefins, polystyrenes, vinyl polymers, acrylic polymers and copolymers and blends thereof.

37. An additive for polymers and a method of improving the reheat characteristics of a polymer or polymeric compositions, the use of an inorganic material to improve the reheat properties of a polymer or polymeric composition, a thermoplastic moulding composition and a moulded article substantially as herein described with reference to the accompanying examples.

ABSTRACT

According to the present invention, there is provided a polymer additive for improving the reheat characteristics of a polymer or polymeric composition, the additive comprising an inorganic material that is not a black carbon, metallic antimony, iron oxide or copper chromite, said additive being present with the polymer prior to reheating. The present invention also relates to a method of improving the reheat characteristics of the polymer and is particularly useful in the field of plastics injection moulding.

Figure 1Figure 2